

and a density value for aragonite of 2.944 g/cm³ (9), is 0.88 ± 0.11 cal/mole deg C. This value is in fair agreement with the values of 0.74 and 1.0 ± 0.5 given by Backstrom and Anderson, respectively (1).

The chief geological application of the calcite-aragonite equilibrium curve is in the interpretation of aragonite formed during metamorphism. Occurrences have been reported in the glaucophane schists of California, both in the Ward Creek area and throughout 140 square miles of Franciscan rocks of the Pacheco Pass area, and in New Zealand along the contact between ultramafic rocks and Permian sedimentary and volcanic rocks (10). Revision of the curve to higher pressures implies a somewhat greater depth of burial for the formation of aragonite. A minimum depth of about 18 km is indicated by our data for the stable formation of aragonite rather than calcite, both of pure CaCO₃. Because the solubility of MgCO₃ (and probably other related components) in calcite is appreciable at high temperatures (7), the equilibrium curve for solid-solution calcite will be somewhat lower than our present curve (11).

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Deuterated Water Effects on Acid Ionization Constants

Abstract. Linear relations of the form

$$\Delta pK = pK^D - pK^H = a + b pK^H$$

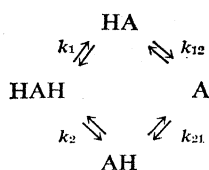
relating ionization constants of acids in light and heavy water must have the same slope b for any kind of acid unless the previously unconsidered charge type is important or this equation is not valid.

The difference between the logarithms of acid-ionization constants in normal and heavy water at comparable ionic strengths and temperature has been represented (1, 2) by a linear equation of the form

$$\Delta pK = pK^D - pK^H = a + b pK^H. \quad (1)$$

Such an equation has been applied (2) to carboxylic acids and ammonium ions with different values of b for each kind of acid group. In this report it is shown that such a result is internally inconsistent when the requirements of ionizations from a dibasic acid are considered.

Consider the general case of a dibasic acid with any kind of acid groups and of any type of charge which ionizes by two paths



If the charge on species HAH is x , the charge on species HA and AH is $(x-1)$ and the charge on A is $(x-2)$. The last subscript on k refers to the group from which a hydrogen is being removed.

By titration of a dibasic acid the two acid ionization macroconstants determined are by definition

$$K_1 = (H^+)[(HA) + (AH)]/(HAH)$$

$$K_2 = (H^+)(A)/[(HA) + (AH)]$$

Four ionization microconstants, one for each of the four depicted equilibria, may also be defined, $k_1 = (H^+)(HA)/(HAH)$, and so forth. The two macroconstants are related to the four microconstants by

$$\begin{aligned} K_1 &= k_1 + k_2 \\ K_2^{-1} &= k_{12}^{-1} + k_{21}^{-1} \\ K_1 K_2 &= k_1 k_{12} = k_2 k_{21} \end{aligned} \quad (2)$$

To determine all four microconstants one more item of information in addition

to the values of the two macroconstants is required (3) but this is not our concern here.

In logarithmic form Eq. 2 is

$$pK_1 + pK_2 = pk_1 + pk_{12} = pk_2 + pk_{21} \quad (3)$$

from which

$$pk_1 - pk_{21} = pk_2 - pk_{12} \quad (4)$$

These equations may be written for ordinary hydrogen or deuterated solvents. For the above dibasic acid the difference in sums of the logarithms of the ionization constants in deuterated and normal water is

$$\begin{aligned} \delta &= pK_1^D + pK_2^D - (pK_1^H + pK_2^H) \\ &= pk_1^D + pk_{12}^D - (pk_1^H + pk_{12}^H) \end{aligned} \quad (5)$$

$$= pk_2^D + pk_{21}^D - (pk_2^H + pk_{21}^H) \quad (6)$$

where the last two equalities follow from Eq. 3. No assumptions have been made so far; the two ionizing groups may be the same or quite different. For instance, HAH may represent a dicarboxylic acid, a diammonium ion, or an amino acid such as glycine where one acid group is a carboxylic acid and the other a substituted ammonium ion.

Assume that Eq. 1 is valid for an acid of any charge type. Apply Eq. 1 to each of the two ionizing groups in Eqs. 5 and 6 regardless of the net charge on the molecule to obtain

$$\delta = a_1 + b_1 pk_1^H + a_2 + b_2 pk_{12}^H \quad (7)$$

$$= a_2 + b_2 pk_2^H + a_1 + b_1 pk_{21}^H \quad (8)$$

When equated, the a terms of Eqs. 7 and 8 cancel, yielding

$$b_1 (pk_1^H - pk_{21}^H) = b_2 (pk_2^H - pk_{12}^H).$$

Substitution from Eq. 4 yields

$$b_1 = b_2$$

We conclude that if the linear relation (Eq. 1) is valid for ionizations from acids of any charge type, the slopes are the same for any kind of acid group. Hence nonidentical slopes (2) obtained from equations of the form of Eq. 1 for carboxylic acid and ammonium ionizations of any type of charge are inconsistent. If we are not willing to accept identical slopes, either type of charge is important or the linear relation of Eq. 1 is not valid. Acid-charge type has not been explicitly considered before and it does seem to be a factor in determining ΔpK . Any linear relation is of course approximate and deviations might be ascribed to a terms in Eq. 1 arising from unusual

hydrogen bonding and other effects. A review of available results (1, 2, 4) indicates that

$$\Delta pK = pK^D - pK^H = 0.45 + 0.015 pK^H \quad (9)$$

is an approximate representation for $-5 < pK < 16$ with wide aberrations on both sides of the line. From $-5 < pK < 16$ all recorded values are within $0.15 < \Delta pK < 0.8$. Ionizations from carboxylic acids with positive charges such as glycine fall below the line while those with negative charges lie above the line of Eq. 9. Since H_2O is a 5 times stronger acid than D_2O , it also lies near the line of Eq. 9, but the 1.5 times greater acidity of H_3O^+ over D_3O^+ (5) falls far below the line and is nearly the lowest ratio recorded.

Some of the greatest deviations from the line of Eq. 9 are given by carboxylic acid ionizations. By explicitly considering charge type and adding a term to Eq. 9, agreement with observed values is markedly improved. For carboxylic acid ionizations only, Eq. 10 is suggested, where Z denotes the net charge on the acid form of the conjugate acid-base pair that is being considered.

$$\Delta pK' = 0.45 + 0.015 pK^H - 0.12Z \quad (10)$$

For instance, for three ionizations from citric acid (2), $pK_1^H = 2.95$, $pK_2^H = 4.38$, and $pK_3^H = 5.80$. From Eq. 9, $\Delta pK_1 = 0.49$, $\Delta pK_2 = 0.52$, and $\Delta pK_3 = 0.54$. Equation 10 gives $\Delta pK_1' = 0.49$, $\Delta pK_2' = 0.64$, and $\Delta pK_3' = 0.78$, in much better agreement with the observed differences (2) of 0.49, 0.64, and 0.75, respectively. Neutral acids such as acetic acid which are nearly on the line of Eq. 9 give, of course, the same difference when Eq. 10 is used. If an equation of the form of Eq. 10 had been used in place of Eq. 1 for carboxylic acid ionizations, the same result, $b_1 = b_2$, would have been obtained if both ionizations were from carboxylic acid groups because terms in Z and $(Z-1)$ would cancel. The numerical value of the "pre- Z " factor, 0.12 in Eq. 10, may be dependent on ionic strength. The ΔpK values for citric acid quoted are at about 0.1 ionic strength. It would be of interest to learn the differences upon extrapolation to zero ionic strength.

No numerical values of charge-type factors, such as appear in Eq. 10 for carboxylic acids, are suggested for other acidic groups because fewer results with a variation in charge type have been recorded. The limited data suggest,

however, that the numerical value would be less for ammonium ionizations. It is suggested that charge-type factors will prove important only where charge separations occur as in carboxylic acid and phenol ionizations and not in proton transfers such as occur in ammonium ions. Substitution of Eq. 10 for carboxylic acid ionizations and Eq. 9 or some other equation with a zero or lesser "pre- Z " factor than Eq. 10 for ammonium ionizations in molecules such as glycine with two different acidic groups yields nonequal slopes differing by the difference of their "pre- Z " factors, for the two kinds of acid groups. Too few points are available to test this hypothesis, but all points for such carboxylic acid ionizations lie below the line of Eq. 9. As an example, for the carboxylic acid ionization from glycine with a positive charge on the acidic form of the molecule and $pK_1^H = 2.47$, application of Eq. 10 yields

$$pK_1 = 0.45 + 0.04 - 0.12 = 0.37,$$

which compares favorably with the observed (2) value of 0.39. For the ammonium ionization from glycine from a

molecule with $pK_2^H = 9.65$ we apply Eq. 9 to obtain $pK_2 = 0.45 + 0.15 = 0.60$ in good agreement with the observed (2) value of 0.63. For triglycine, however, with $pK_1^H = 3.28$ Eq. 9 gives better agreement with the experimental difference (2) of 0.47 indicating that charge separation also plays a role in determining ΔpK .

Even though this last section has emphasized a probable role for charge type in determining ΔpK , many other factors such as bond type undoubtedly enter this complex quantity (6).

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Alkanes in Natural and Synthetic Petroleums: Comparison of Calculated and Actual Compositions

Abstract. A similarity exists between the low molecular weight alkane isomers in crude oil and Fischer-Tropsch catalytic synthesis products. The composition of the C_4 through C_7 alkane isomers in a crude oil was calculated quantitatively with the equations previously used to calculate the alkane isomers in Fischer-Tropsch products. These results may have significance in ascertaining the origin of the volatile hydrocarbons in crude oils.

Practically all present hypotheses on the origin of petroleum propose that the source materials were the remains of plants and animals (1). Early experiments pointed to inorganic origins in the earth (2). These theories have been mainly displaced, but proponents still exist (3, 4). Robinson (4) has proposed that petroleum consists of primeval oils of unknown source that became admixed with oils from organic life. The proposed primeval oils might possibly have arisen by catalytic syntheses such as the Fischer-Tropsch synthesis. This is a catalytic reaction of CO and H_2 at about 170° to 330°C at atmospheric or higher pressures, that produces complex mixtures of hydrocarbons and oxygenated derivatives from C_1 to waxes of high molecular weight. The hydrocarbons include paraffins, olefins, naphthenes, and aromatics.

We have noted a similarity between the concentrations of the alkane isomers in crude oils (5, 6) and the concentrations in hydrogenated Fischer-Tropsch synthesis products (7-11). Table 1 (i) illustrates this similarity for the C_6 and C_7 branched alkanes. In both products a reversal occurs for the methyl derivatives: the concentration of 2-methylpentane is greater than that of 3-methylpentane, and the concentration of 2-methylhexane is less than that of 3-methylhexane. Recent data from 11 of 14 crude oils examined also show this reversal (12). One of the unique results found in the analysis of Fischer-Tropsch products (7, 8) was this same reversal.

The comparison of Fischer-Tropsch and petroleum components in Table 1, (i) is not very quantitative. Unfortunately there are no detailed analyses of